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Mechanistic aspects of hydrodeoxygenation of *p*-methylguaiacol over Rh/silica and Pt/silica.

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Abstract.

The mechanism of p-methylguaiacol (PMG) hydrodeoxygenation has been examined over two Rh/silica catalysts and a Pt/silica catalyst at 300 °C and 10 barg. The mechanism has been determined as a sequential conversion of PMG to 4-methyl catechol to m- and p-cresol to toluene, although direct conversion of PMG to p-cresol is also favoured over the Rh/silica (JM) catalyst. Dehydroxylation and hydrogenation have been shown to occur over the metal function, while demethylation and demethoxylation take place on the support.

Introduction.

The subject of bio-oil hydrodeoxygenation (HDO) is a highly active research area [1,2] and it is a one of the methodologies used to convert bio-oil into a form that is able to be blended with petroleum. In a previous paper [3] we examined the deactivation of three catalysts used for the HDO of *para*-methylguaiacol. Three catalysts were studied: 2.5% Rh/silica supplied by Johnson Matthey (JM), 2.5% Rh/silica (A) and 1.55% Pt/silica both prepared in-house. All three showed initial deactivation but the Rh/silica (JM) achieved steady-state after ~6 h on-stream and maintained a constant activity over the test period. In contrast the other two catalysts did not reach steady state within the timeframe of the tests. The Rh/silica (A) and Pt/silica showed continuous deactivation over the test period but the mode of deactivation was different for each catalyst. [3] In this paper we turn our attention to the mechanisms of the reaction over the different catalysts and how these change with deactivation. There are no other studies of *p*-methylguaiacol in the literature however guaiacol has been the subject of a number of investigations. Mu *et al*. [4] studied HDO of guaiacol over a Rh/C catalyst at 40 bar hydrogen and 250 °C in a batch process. They reported that demethoxylation was the dominant process with phenol as the main product (~ 35 % selectivity) with a conversion of ~13 %. The other major products were cyclohexanone and cyclohexanol (~25 % selectivity). Gutierrez *et al*. [5] examined rhodium and platinum supported on zirconia catalysts for guaiacol HDO at 100 °C and found principally hydrogenated products. At 300 °C more HDO than hydrogenation was observed, although no details were given. Over platinum catalysts there has been slightly more research and some consideration of the mechanism. The study by Gates and co-workers [6] reveals a detailed network for the conversion of guaiacol over Pt/alumina, where a large number of products were detected, some by HDO, some by transalkylation and some by hydrogenolysis. In the course of our previous work it was clear

that the activity of the catalysts for demethylation, demethoxylation and hydrogenation were affected differently by the catalyst deactivation and we were interested to put this in context mechanistically and by using two metals and two silica supports possibly determine the sites for the different reactions.

Results and Discussion.

The three catalysts were tested over an extended period. As reported previously the Rh/silica (A) and the Pt/silica both showed deactivation behaviour, whereas the Rh/silica (JM) catalyst achieved a steady state within the timeframe of the testing. Figures 1-3 reveal the selectivity at 1 h and 32 h on stream for all catalysts. It can be seen that there is a significant shift in selectivity with the Rh/silica (A) and a less dramatic but still noticeable shift for the Pt/silica. The selectivity obtained from the Rh/silica (JM) catalyst is relatively constant over the time period.

At this point it is worth noting the bond strengths of the different species. The ArO-CH_3 bond strength is ~381 kJ.mol^{-1}, the Ar-OCH_3 bond strength is ~419 kJ.mol^{-1}, the Ar-OH bond strength is ~431 kJ.mol^{-1}, while the Ar-CH_3 bond strength is ~389 kJ.mol^{-1}.

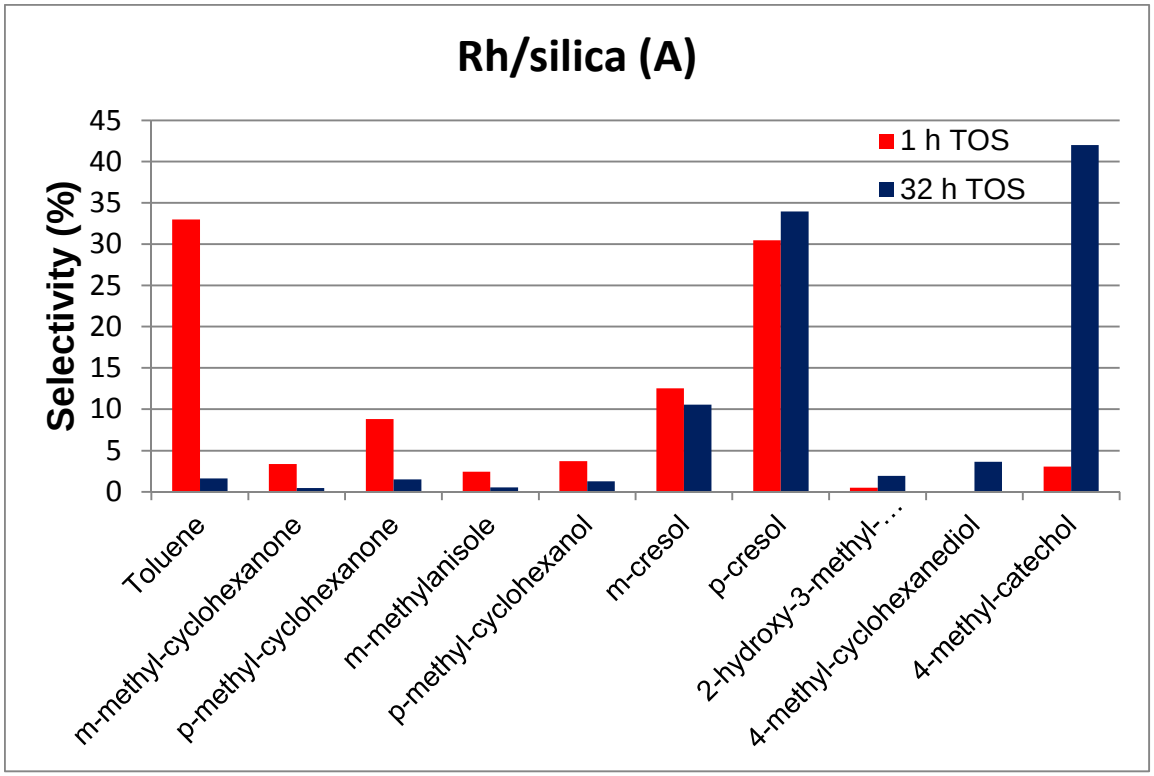


Figure 1. Catalyst Rh/silica (A); selectivity at 1 h (conv 50 %) and 32 h (conv. 26 %) time on stream.

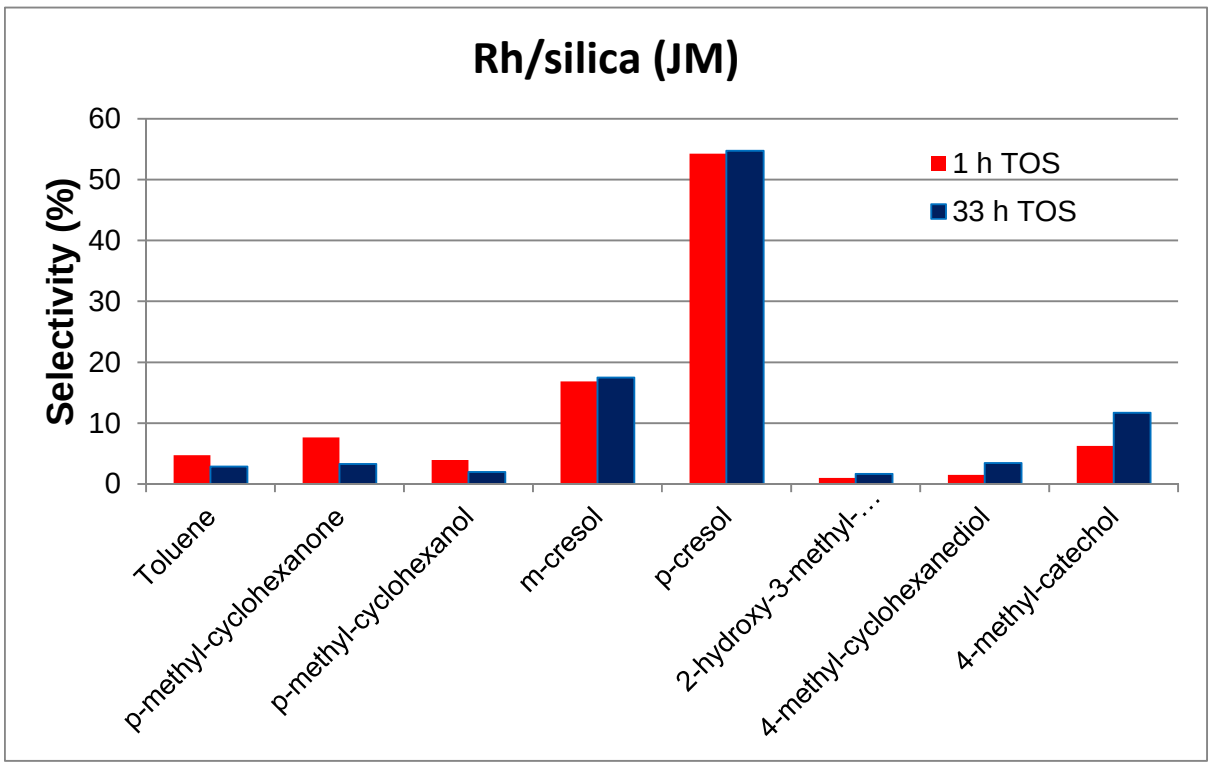


Figure 2. Catalyst Rh/silica (JM); selectivity at 1 h (conv. 47 %) and 32 h (conv. 34 %) time on stream.

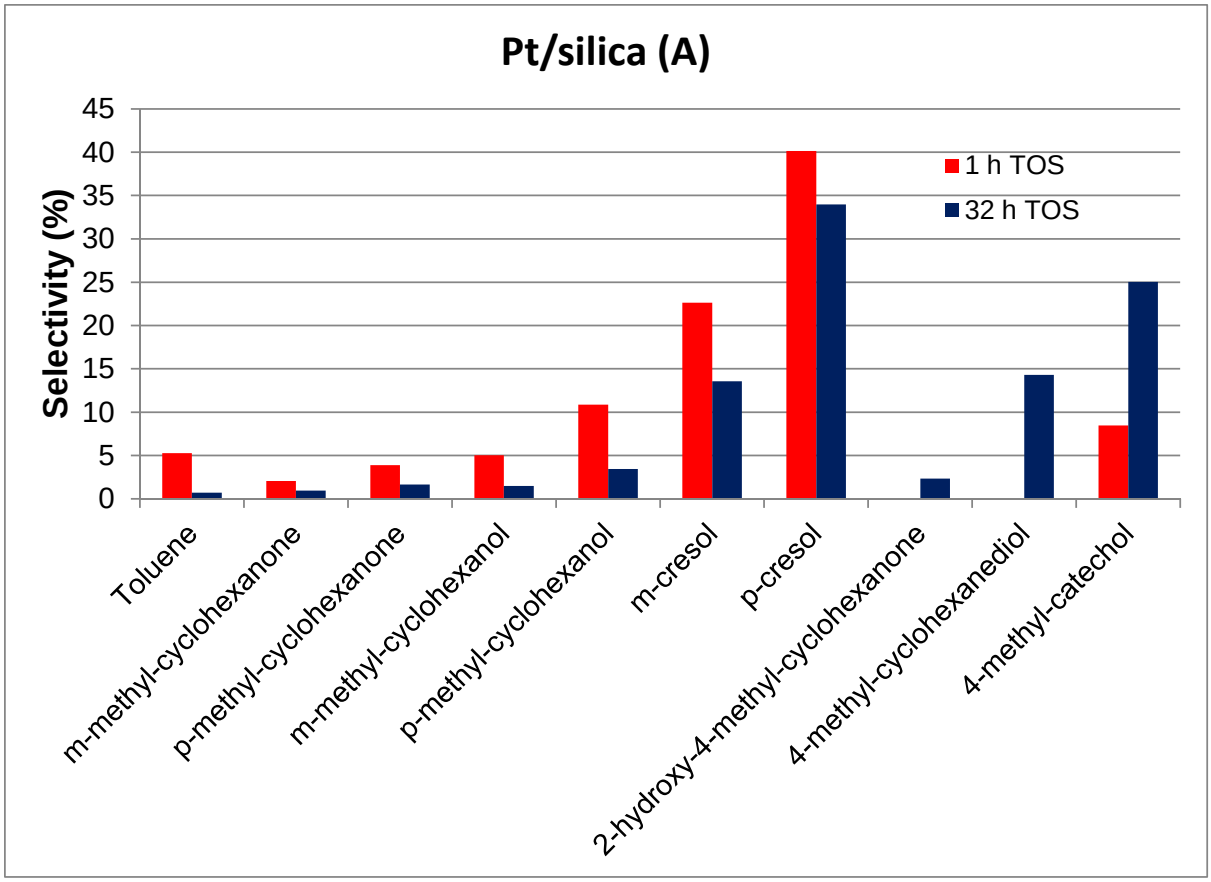
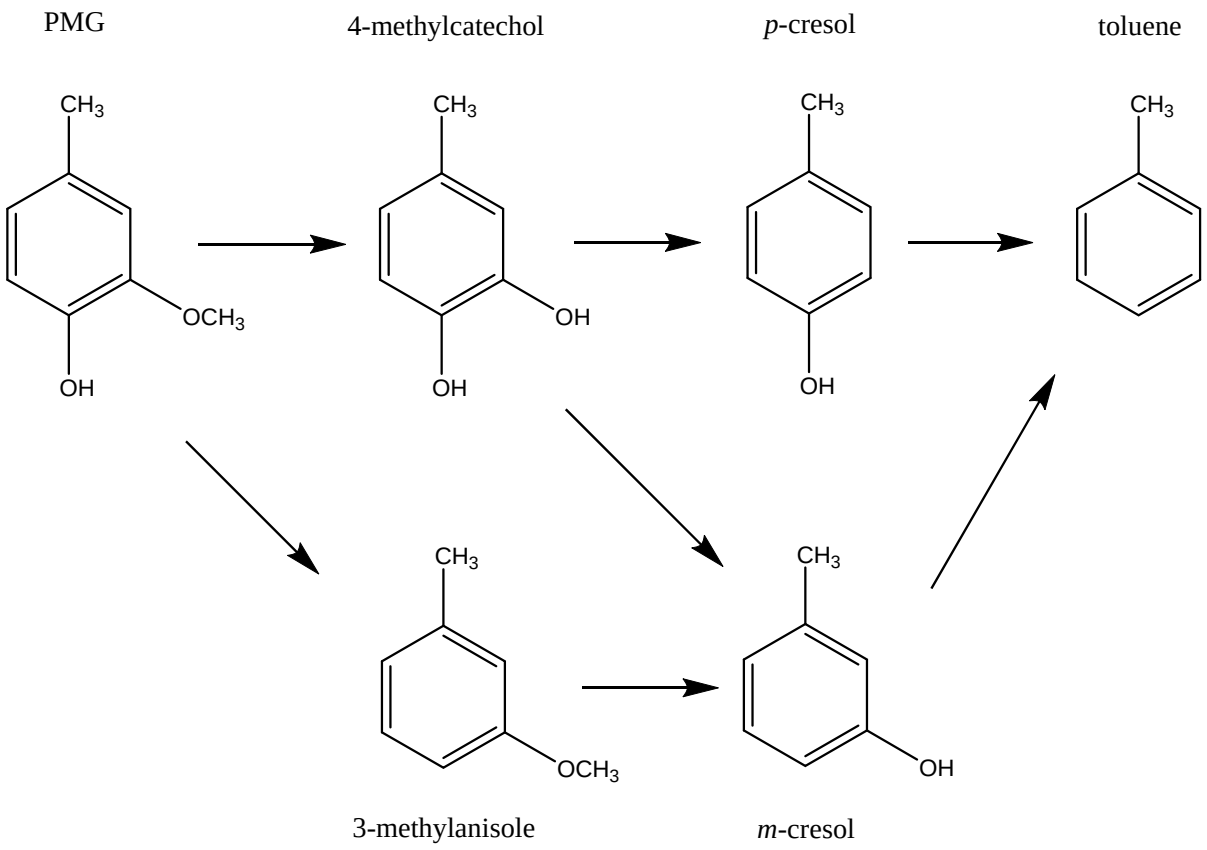


Figure 3. Catalyst (Pt/silica) selectivity at 1 h (conv. 70 %) and 32 h (conv. 47 %) time on stream.

In the early stages of the test the Rh/silica (A) is selective to toluene and *para*-cresol but after 32 h time on stream the main products are *para*-cresol and 4-methylcatechol. Mechanistically we can understand this as a sequential hydrogenolysis as shown in Scheme A. Initially the highly active catalyst can hydrogenolyse all the C-O bonds to produce toluene. Note that we saw no evidence for C-C bond scission and the generation of benzene. Hydrogenation products of the cresols (*p*- and *m*-methylcyclohexanone) were observed but not methylcyclohexane. As the catalyst deactivates however the high hydrogenolysis/HDO activity is lost and the system retreats back through the intermediates such that after 32 h, the main products are *p*-cresol and 4-methycatechol. Interestingly 3-methylanisole selectivity

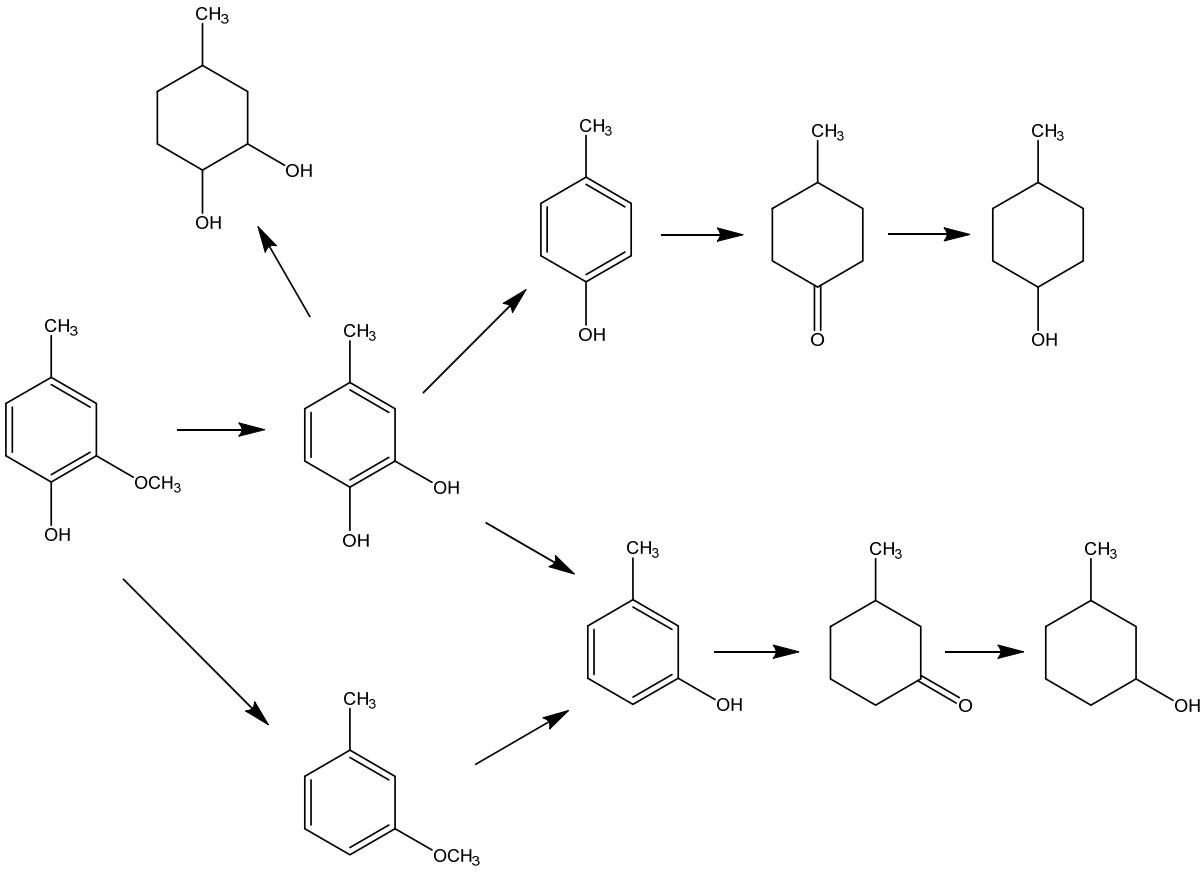


Scheme A. Mechanism of hydrogenolysis/HDO of PMG to toluene over Rh/silica (A).

decreases suggesting that dehydroxylation of PMG to 3-methylanisole and then on to m-cresol is not a major pathway. Demethylation of PMG to 4-methylcatechol and demethoxylation to p-cresol are much less affected as may be expected from the bond strengths.

In contrast, the Rh/silica (JM) catalyst shows no high hydrogenolysis/HDO activity related to removing all the hydroxyl groups but stops with one hydroxyl remaining (toluene selectivity < 5 %). It is possible that the absence of these higher activity sites helps reduce catalyst deactivation. The changes in selectivity are slight for the Rh/silica (JM) but they are consistent with Scheme A.

In slight contrast the Pt/silica catalyst shows more hydrogenation activity. At 1 h time on stream the main products with the Pt/silica catalyst are *m*-cresol and *p*-cresol, similar to that found with the Rh/silica (JM) catalyst. However there is also significant selectivity to the hydrogenated form of both cresols. If we sum the selectivity for *p*-methylcyclohexanone and *p*-methylcyclohexanol, then we achieve a figure of ~15 % with proportionally lower values for the *meta*-isomers. After 32 h, when the catalyst has deactivated, the selectivity changes to favour 4-methylcatechol and 4-methyl-2-hydroxy-cyclohexanol. Note that even though the activity has decreased the yields of 4-methyl-2-hydroxy-cyclohexanol and 4-methyl-2-hydroxy-cyclohexanone have increased, whereas the yields of *m*-cresol and *p*-cresol do decrease with conversion. A description of the reaction mechanism for Pt/silica is shown in Scheme B.



Scheme B. Mechanism of hydrogenolysis/HDO of PMG over Pt/silica.

The above discussion considers the behaviour of the catalysts with time and changes in their selectivity; however it is also worthwhile to compare the selectivity at equivalent conversion. The results are shown in Figure 4. What is immediately noticeable is that the yield/selectivity of 4-methycatechol is the same for both Rh/silica (A) and Pt/silica, the catalysts with the same support. This suggests that the demethylation reaction (the breaking of the ArO-CH_3 bond) takes place over the support rather than the metal function. In contrast dehydroxylation (breaking Ar-OH bonds) appears to take place over the metal function. This is suggested at by the selectivity of toluene, where the Rh catalysts give a similar figure but is confirmed by the selectivity to *m*-cresol and *m*-anisole (Rh/silica (JM) and Rh/silica (A) selectivity 0.6 %, Pt/silica selectivity 0.4 %). This in agreement with Nimmanwudipong *et al*. who suggested dehydroxylation was performed over the metal function [6]. It is also

consistent with the deactivation study, where demethylation activity was the least affected by carbon deposition [3]. There are two routes to the formation of *p*-cresol, through 4-methylcatechol by dehydroxylation and by demethoxylation direct from PMG. Given that dehydroxylation is a difficult process, the high selectivity to *p*-cresol over the Rh/silica (JM) suggests that demethoxylation of PMG to give *p*-cresol takes place over the support.

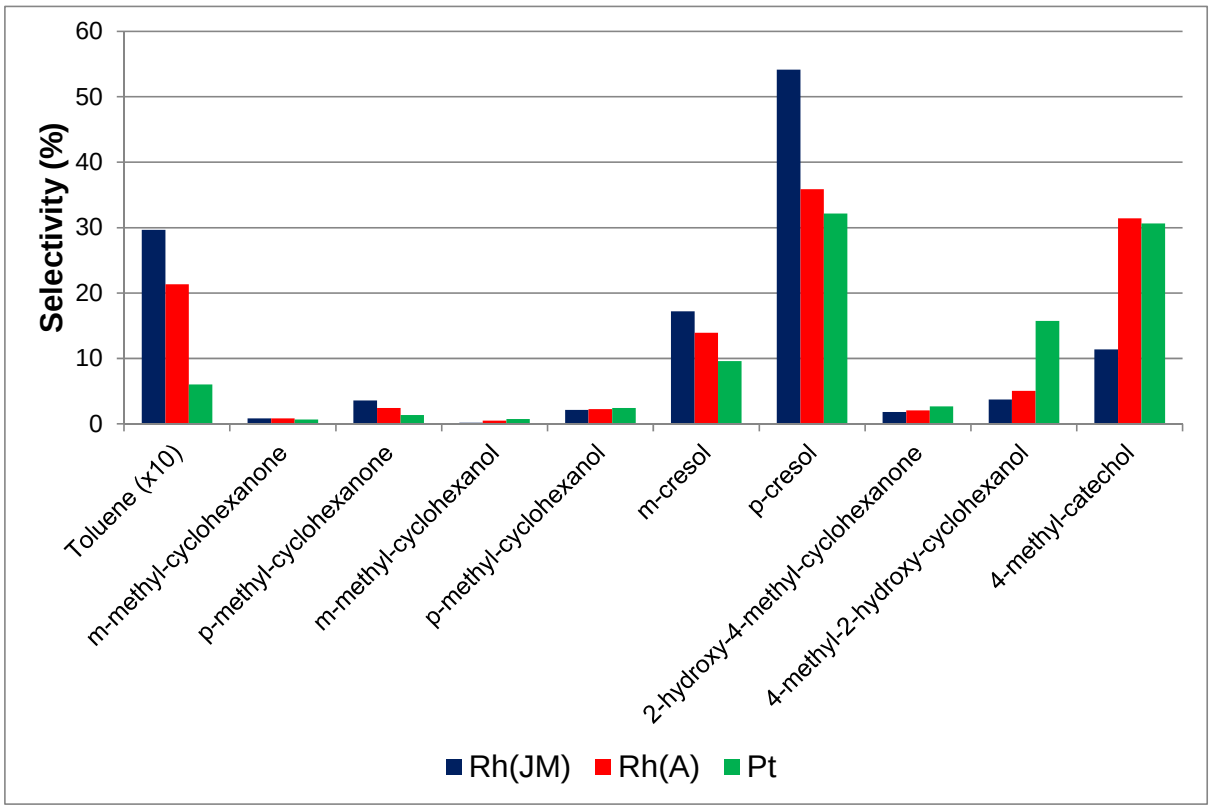


Figure 4. Selectivity to products at ~32 % conversion.

Experimental

Three catalysts were used in this study 2.5 % Rh/SiO_2 (JM), 2.5 % Rh/SiO_2 (A) and 1.55 % Pt/SiO_2. All catalysts were prepared by impregnation and details of their preparation is reported elsewhere [3]. The catalysts were ground and sieved to between 350 and 850 μm

before use and all reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

Conversion and yield are defined in equations 1, 2 and 3

Conversion = ((Σ moles products + moles PMG out)-(moles PMG out))/(Σ moles products + moles PMG out) (Equation 1)

Selectivity = moles product/Σ moles products (Equation 2)

Yield = moles product/(Σ moles products + moles PMG out) (Equation 3)

The catalytic testing and analysis methodology has been reported elsewhere [3] but briefly the tests were performed in a continuous-flow, fixed-bed reactor. The catalysts (~0.5 g) were pre-reduced *in-situ* before reaction at 300 °C for 2 h under 100 mL min^{-1} of 40 % H_2/Ar. After the catalysts were reduced, *p*-methylguaiacol (PMG) was pumped into the gas flow and vaporised at 200 °C. The reaction temperature was 300 °C with a hydrogen partial pressure of 4 barg giving a H_2:PMG ratio of 15. The total pressure was made up to 10 barg using argon. Typical weight hourly space velocity (WHSV) of PMG was 2.5 h^{-1}, while the gas hourly space velocity (GHSV) was 7200 h^{-1}. The products were trapped in a condenser at 5 °C before sampling.

A full description of the analysis methodology is reported elsewhere [3]. In brief to fully quantify the products three distinct solutions were prepared from the same mixture of products. Firstly two internal standards were added, (decane at 0.86 and heptadecane at 10.2 g L^{-1}) before two aliquots were silylated. Analysis of the three solutions using this technique permitted a full quantification of minor and major products. The quantitative analyses were performed on an HP 5890 gas chromatograph fitted with a Supelco DB-5 capillary column (30m × 0.32 mm, 1 mm thickness).

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